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POLYPROPYLENE PROCESSING WITH REDUCED CYCLE TIME IN
INJECTION-STRETCH-BLOW MOULDING.

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This invention relates to the field of polypropylene processing in injection -stretch-blow-moulding and discloses the use of metallocene -prepared polypropylene for reducing the cycle time while improving the optical properties of the finished product.

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Presently, the most common material used in injection -stretch-blow-moulding is polyethylene terephthalate (PET). It has the advantage of achieving very short cycle time of the order of 1000 to 1500 bottles per cavity per hour and it offers the further advantage of having excellent optical properties. It suffers from the

15 considerable disadvantage of being very costly.

Alternatively other thermoplastic materials such as for example polyvinylchloride (PVC), polystyrene, acrylonitrile, polypropylene and acetals could be used.

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Among those, polypropylene prepared with a Ziegler -Natta catalyst system has been used with reasonable success. The cycle time, although honorable, is nevertheless higher than that of PET resins and the optical properties, although reasonably good do not reach the level of those obtained with the PET resins.

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There is thus a need to replace the costly PET resins with other resins that will not suffer from the disadvantages of the polypropylene prepared with a Ziegler -Natta catalyst system.

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It is an aim of the present invention to provide resins that are processed in injection-stretch-blow-moulding with a very short cycle time.

It is another aim of the present invention to provide resins having excellent optical properties.

5 It is a further aim of the present invention to provide resins that have a very high rigidity.

It is also an aim of the present invention to provide resins that have an excellent chemical resistance.

10 It is yet another aim of the present invention to provide articles that can be filled with hot liquids.

It is yet a further aim of the present invention to provide resins that offer good impact and compression properties.

15 It is also an aim of the present invention to prepare articles having good barrier properties.

20 Accordingly, the present invention discloses the use of metallocene -produced polypropylene to prepare single layer or multi -layer articles by injection -stretch blow moulding with a reduced cycle time, said article having excellent optical properties and rigidity.

25 The metallocene-produced polypropylene used in the present invention is preferably an isotactic homopolymer or random copolymer of propylene. It has a melt index of from 2 to 100 g/10 min and preferably of from 10 to 20 g/10 min. The amount of ethylene present in the resin is of from 0 to 10 wt%, preferably of from 0 to 4 wt%.

30 The melt flow index MFI is measured using the procedures of standard test ISO 1133 at 230 °C for polypropylene resins and under a load of 2.16 kg.

The metallocene component used to prepare the isotactic homopolymer or random copolymer of propylene can be any bridged metallocene known in the art, represented by the general formula I:

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wherein (CpR'_k) is a cyclopentadienyl or substituted cyclopentadienyl, each R' is the same or different and is hydrogen or a hydrocarbyl radical such as alkyl, alkenyl, aryl, alkylaryl, or arylalkyl radical containing from 1 to 20 carbon atoms or two carbon atoms are joined together to form a C₄-C₆ ring, wherein $(C'pR'''_k)$ is a cyclopentadienyl, or an indenyl or a fluorenyl, substituted or unsubstituted, wherein R''' is the same or different and is hydrogen or a hydrocarbyl radical such as alkyl, alkenyl, aryl, alkylaryl, or arylalkyl radical containing from 1 to 20 carbon atoms, and wherein the substituents on the Cp rings are selected to impart C₁ or C₂ symmetry to the compound; R'' is a structural bridge between the Cp and the Flu rings to impart stereorigidity that can be a C₁-C₄ alkylene radical, a dialkyl germanium or silicon or siloxane, or a alkyl phosphine or amine radical; Q is a hydrocarbyl radical such as aryl, alkyl, alkenyl, alkylaryl, or aryl alkyl radical having from 1-20 carbon atoms, hydrocarboxy radical having 1-20 carbon atoms or halogen and can be the same or different from each other, and M is a metal Group IVb of the Periodic Table. Preferred metals are Zr, Ti, Hf.

Preferably, $(C'pR'''_k)$ is an unsubstituted fluorenyl. Among the preferred metallocenes used in the present invention, one can cite among others isopropylidene-(3-tert-butyl-5-methyl-cyclopentadienyl)(fluorenyl) zirconium dichloride for the production of isotactic random copolymer of propylene.

The metallocene may be supported according to any method known in the art. In the event it is supported, the support used in the present invention can be any organic or inorganic solids, particularly porous supports such as talc, inorganic

oxides, and resinous support material such as polyolefin. Preferably, the support material is an inorganic oxide in its finely divided form.

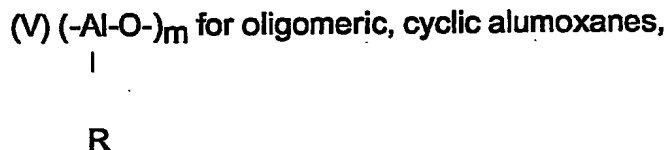
The addition on the support, of an agent that reacts with the support and has an
5 ionising action, creates an active site.

Preferably, alumoxane is used to ionise the catalyst during the polymerisation procedure, and any alumoxane known in the art is suitable.

10 The preferred alumoxanes comprise oligomeric linear and/or cyclic alkyl alumoxanes represented by the formula :



15 and



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wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C_1 - C_8 alkyl group and preferably methyl.

Methylalumoxane is preferably used.

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One or more aluminiumalkyl(s) can be used as cocatalyst in the reactor. The aluminiumalkyl is represented by the formula AlR_x can be used wherein each R is the same or different and is selected from halides or from alkoxy or alkyl groups having from 1 to 12 carbon atoms and x is from 1 to 3. Especially
30 suitable aluminiumalkyl are trialkylaluminium, the most preferred being triisobutylaluminium (TIBAL).

Further, the catalyst may be prepolymerised prior to introducing it in the reaction zone and/or prior to the stabilization of the reaction conditions in the reactor.

- 5 The injection-stretch-blow-moulding can be carried out either in a two-step process or in a single step process. The two-step process is generally preferred and it is carried out in two separate locations. It comprises the steps of:
- providing a preform by injection moulding on a multi-cavity mould;
 - cooling the preform to room temperature;
 - 10 - transporting the preform to the blow moulding machine;
 - reheating the preform in the blow moulding machine in a reflective radiant heat oven;
 - passing the heated preform through an equilibrium zone to allow the heat to disperse evenly through the preform wall;
 - 15 - stretching the preform axially by a centre rod ;
 - orienting the stretched preform radially by high pressure air.

In this process, the stretching step is the critical step, as it requires reheating of the preform: optimisation of the preform is thus required. The preform is reheated
20 to a temperature that is about 10 °C lower than the fusion temperature of the resin.

The articles prepared according to the present invention are hollow containers and bottles that can be used in various food and non-food applications. The food
25 applications comprise the storage of water, juices, oil, flavoured still and carbonated beverages, isotonic drinks, dry products and fresh milk. The non-food applications comprise the storage of cosmetic and pharmaceutical products, dishwashing or washing detergent and dry products.

30 The bottles and hollow containers prepared according to the present invention have excellent optical properties, very good impact strength. They also have a

compression strength that is much larger than both the bottles prepared with PET resins and conventional polypropylene resins prepared with Ziegler -Natta catalyst system.

- 5 The cycle time for preparing the articles according to the present invention is substantially shorter than that necessary with Ziegler -Natta (ZN) polypropylene: it is at least 10% shorter, preferably 15 % shorter than the cycle time of ZN resins. It is comparable to that of PET resins. The use of metallocene catalyst systems allows the production of polypropylene resins having a low fusion point, while
- 10 keeping good mechanical properties of strength, compression and impact, as well as improved optical properties. The rigidity of the finished articles is increased by at least 3% with respect to that of ZN -prepared articles and by at least 20 % with respect to that of PET -prepared articles. The optical properties are equivalent to those of PET -prepared articles and the haze is improved by at
- 15 least 40 % with respect to that of articles prepared with a ZN catalyst system.

Examples.

Two preform designs were used in the examples:

- 20 - Design 1 was the commercial polyethylene terephthalate (PET) preform design used for the preparation of bottles: it had a weight of 20 g and it is represented in Figure 1.
- Design 2 was the Bekum PP preform design used for the preparation of bottles: it had a weight of 23.8 g and it is represented in Figure 2.

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Three preforms were prepared:

- P1 was prepared from a commercial PET resin R1 with design 1.
- P2 was prepared from a metallocene -produced polypropylene resin R2 with Design 2.
- 30 - P3 was prepared from a Ziegler -Natta polypropylene resin R3 with Design 2.

Resin R2, according to the present invention was a metallocene -prepared random copolymer of propylene and ethylene prepared with a metallocene catalyst system comprising a bridged (3 -tBu-5Me-cyclopentadienyl)(fluorenyl) zirconium dichloride component and an activating agent. It had an MFI of 14g/10 min.

Resin R3 was a classical commercial Ziegler -Natta random copolymer of propylene having a MFI of 10 g/10 min and sold under the commercial name of PPR7220 (previously called PPR3100MT3).

Preform P1 was purchased.

Preforms P2 and P3 were produced on a Synergy 100 injection moulding machine having a 100 tons clamping force and a maximum injection pressure of 1750 bars. The screw had a length L over diameter D ratio L/D of 20, a diameter D of 45 mm, a compression ratio of 1:2 and it was equipped with two cavity moulds.

The moulding conditions for preparing preforms P2 and P3 are summarised in Table I.

TABLE I.

		units	P2	P3
plasticising	screw rotation speed	rpm	100	100
	back pressure	bar	50	50
	set melt temperature	°C	211	211
	dosing time	s	4.22	4.02
injection	injection time	s	2.12	2.69
	maximum injection pressure	bar	435	435
	pressure at switch-over	bar	426	426
holding	cushion	mm	2.6	3
	switch-over point	mm	4.4	4.3
	holding pressure	bar	359	359
	holding time	s	8.5	6.29

- 5 Each preform was then used to prepare 0.5 l bottles on a two-cavity linear injection-stretch-blow-moulding (ISBM) machine ADS G62.

These bottles were tested for cycle time, optical and mechanical properties and the results are displayed in Table II.

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Bottles B1 to B3 were prepared respectively from preforms P1 to P3 and bottle B4 was a commercial Vittel bottle.

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TABLE II.

Bottle	Cycle time (b/h/cavity)	Rigidity (N)	Impact drop height (m)	Optical properties (%)	Visual transparency
B1	1500	120	>6 m	9.8	+
B2	1375	165	>6 m	10.3	+
B3	1250	160	>6 m	15.7	-
B4	n.a.	100	>6 m	n.m.	+

n.a. means: not available,

n.m. means: not measured.

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The compression test used to measure the rigidity followed the method of standard test ASTM 2659 -95 on a Zwich tensile machine operated at a velocity of 10 mm/min.

- 10 The impact drop strength was measured by a drop test developed in house and based upon a UN norm and standard test ASTM 2463 -95. The bottles were filled at 95 % with water and conditioned at room temperature (about 25 °C) for 48 hours and then were dropped on the bottom from increasing heights. The height was increased stepwise until rupture occurred. In the present test, the maximum
- 15 drop height of 6 metres that could be measured with the equipment was reached without recording any ruptures.

- The haze was measured following the methods of standard test ISO 14782 but it must be noted that the bottle design is not suitable for recording reliable and
- 20 reproducible measurements. The same remark applies to the optical properties that are indicative in the present examples.